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THE EFFECTS OF TEMPERATURE AND SOLVENT COMPOSITION ON THE SEPARATION OF POLYNUCLEAR AROMATIC HYDROCARBONS ON BOTH A LIQUID CRYSTAL STATIONARY PHASE AND A VYDAC 201TP C_{18} STATIONARY PHASE

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ABSTRACT

THE EFFECTS OF TEMPERATURE AND SOLVENT COMPOSITION ON THE SEPARATION OF POLYNUCLEAR AROMATIC HYDROCARBONS ON BOTH A LIQUID CRYSTAL STATIONARY PHASE AND A VYDAC 201TP C_{18} STATIONARY PHASE

by Mary M. Miller

Two stationary phases were tested for retention of polynuclear aromatic hydrocarbons on high-performance liquid chromatography. A bonded nematic liquid crystal stationary phase was utilized, containing the silanized form of 4-[4-(allyloxy)benzoyloxy)biphenyl. A polymeric stationary phase, Vydac 201TP C_{18}, was also examined. Both were tested over the temperature range of 25°C to 70°C, using anthracene and phenanthrene. As the temperature of the stationary phase increased, a decrease in retention was observed, as expected. Both phases showed shape selectivity, supporting the slot theory of retention. Retention based on the planarity of the solute was observed by the polymeric phase, owing to the ordered state of the bonded phase. Mobile phase composition was also varied on the Vydac column. Polarity did exhibit an effect on the retention of anthracene and phenanthrene, the more polar solvent resulting in longer retention times.

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INTRODUCTION

Liquid crystals have been used for many years in the field of analytical chemistry. Their unusual properties allow otherwise difficult separations to be performed. Liquid chromatography (LC), supercritical fluid chromatography (SFC), and gas chromatography (GC) have utilized liquid crystals as stationary phases for the separation of many different compounds.

Liquid crystals have been defined as an intermediate state between the crystalline solid and the amorphous liquid. They spontaneously orient their long axes approximately parallel. This results in a more ordered state where the liquid crystals are aligned parallel to each other. This allows for ease of movement as the molecules slide past one another [1].

The transformation of a liquid crystal from its crystalline state to an isotropic liquid can occur in one or more transitions. These transitions, known as mesophases, can be either thermotropic or lyotropic in nature. Thermotropic crystals exhibit properties between a solid and a liquid, as long as they maintain a temperature that is within a specific range above their melting point. Further heating to the clearing temperature results in an isotropic liquid. Lyotropic crystals are influenced by solvent

interaction. Transformations of these types of crystals occur when two or more components are mixed together [2].

Thermotropic liquid crystals can be divided into three classes. Nematic liquid crystals are arranged approximately parallel along their long axes. The cholesteric structure is a twisted nematic structure, occurring in compounds with chiral centers or in mixtures including a chiral compound. The smectic liquid crystal consists of molecules arranged parallel to each other in layers. This is the most ordered of the liquid crystal structures and can convert between eight different types [2]. The smectic liquid crystal can transform into a nematic or cholesteric liquid crystal upon further heating.

Gas chromatography has utilized the unique characteristics of liquid crystals as a stationary phase to perform many separations [3,4]. Because of its wide mesophase range, the nematic structure is used most frequently. The three primary areas of application have been in separating isomeric organic compounds [5], polynuclear aromatic hydrocarbons [6-10], and optical isomers [11].

Many factors influence retention of the solute on the liquid crystal stationary phase, including the vapor pressure of the solute, dispersion, dipole interactions, and induced dipole interactions. The shape of the solute, as

well as the ordered compact packing of the planar liquid crystal stationary phase, also play an important role in retention [12]. Rod shape solutes have been found to exhibit longer retention times with liquid crystal stationary phases than other shaped isomers [6]. The planarity of the solute also plays an important role in retention.

Markides, et al. [12] found that increasing the spacer length between the mesomorphic group and the polysiloxane backbone generally led to an increase in transition temperature between the mesophase and the isotropic liquid. It was also found that crosslinking of the stationary phase generally lowered the transition temperature. This work demonstrated the ability to affect retention and selectivity by altering the structure of the liquid crystal stationary phase. Haky, et al. [7] showed discontinuity in the curves of the separation factor as a function of temperature. A phase change was proposed to explain this behavior. Solvent can also have a similar effect on retention and selectivity.

Liquid crystals have also been used as the bonded phase in supercritical fluid chromatography. Work done by Jinno, et al. [13] demonstrates the advantages of a liquid crystal stationary phase in the separation of polycyclic aromatic hydrocarbons (PAHs). The results indicate a stronger molecular planarity and shape recognition capability of the

phase than common monomeric and polymeric octadecylsilica (ODS) phases. The highly ordered bonded phase structure of the liquid crystal explained this behavior. The liquid crystal phase was shown to be similar in molecular planarity recognition to the polymeric ODS phase, although the slot established between bonded moieties of the liquid crystal phase appears to be much deeper than the polymeric ODS phase. The density of the mobile phase affected the planarity recognition inversely. Decreasing the temperature induced a more ordered bonded phase such that planarity recognition increased. Modifier addition did not have an appreciable effect on the recognition capability.

The research by Jinno, et al. was performed using SFC. The stationary phase is the most effective parameter to alter for optimization of SFC selectivity. SFC has also been shown to offer higher selectivity than HPLC for molecular planarity of PAHs. SFC was seen to enhance selectivity over HPLC by a factor of two in this particular study.

One of the biggest current areas of research, with respect to liquid crystal stationary phases, is HPLC. This technique wasn't utilized as much in the past as gas chromatography. GC behavior may be very different from HPLC in that the solute molecules are at an essentially infinite dilution, causing no disruption in the molecular ordering of

the liquid crystal. HPLC involves the interaction of solute molecules and their sphere of mobile phase with the stationary phase. The mobile phase also interacts with the stationary phase in HPLC, unlike the inert gas mobile phase used in GC [14].

Previous work has been done in the area of HPLC with liquid crystals as the bonded phase. Two groups of researchers have physically coated the liquid crystal moiety onto a solid support surface [14,15]. This type of stationary phase can lead to short column lifetimes due to solvent interactions and shear forces. Taylor, et al. [14] attempted several methods of coating the support with moderate success. Temperature studies resulted in a dramatic increase in capacity factor for steroid molecules as the temperature of the column increased. This was attributed to a change in the structure of the liquid crystal stationary phase.

Recent work performed by a group of scientists at San Jose State University utilizing liquid crystals as a stationary phase for HPLC has shown promising results. The compound used becomes a liquid crystal when bonded to polysiloxane. The starting material was treated with dimethylchlorosilane to produce a reagent suitable for bonding to a silica surface [16]. The resultant compound, [(4-allyloxy)benzoyloxy]-4-methoxyphenyl (ABMP), was then

characterized by elemental analysis, diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), CP/MAS carbon-13 NMR, and differential scanning calorimetry (DSC).

In addition to the above studies, chromatography experiments were performed to better understand the bonded phase [17]. Various organic solvents (acetonitrile, methanol, and tetrahydrofuran) were used with the liquid crystal stationary phase. The percent of water was varied with each solvent. Two pairs of solutes were evaluated: anthracene and phenanthrene, carvone and pulegone. Both pairs exhibited a linear region with no separation (high solvent strength) and a non-linear region with separation (low solvent strength) on the graphs of log k' vs % organic solvent.

A theory proposed by Nahum, et al. [18] states that interaction of polar solutes with the stationary phase in reverse phase chromatography involves both solvophobic (hydrophobic) interactions as well as silanophilic interactions; silanophilic refers to silanol groups that may be accessible to solute molecules for adsorption at the surface. The theory that silanophilic interactions causes the linear and non-linear portions of the liquid crystal log k' vs % organic solvent graph was ruled out, due to the fact that silanophilic interactions predict a concave log k vs % organic graph [18], and peak shapes were symmetric, as

opposed to tailing in a mixed mode separation. On a conventional C-18 column, it was seen that log k' vs % organic is a straight line for these same two pairs of solutes.

Lochmuller, et al. [19] proposed that collapse of the bonded phase occurs in the presence of a hostile (polar) solvent. This minimizes the surface area in contact with the hostile solvent molecules. This theory was proposed as a possible cause for the linear and non-linear portions of the log k' vs % organic graphs. A gradual transformation is inferred from the slope change, as opposed to a single new value that would result from an immediate phase change.

Additional work has been recently reported that utilizes a liquid crystal bonded phase for separation of PAHs in HPLC, using a microcolumn LC system [20]. The stationary phase was shown to have a strong molecular planarity recognition capability which was attributed to its ordered bonded phase structure. Planar solutes are retained longer, while non-planar solutes are eluted faster. A shape selectivity was also seen for this liquid crystal stationary phase. The water concentration of the mobile phase had an inverse effect on the separation factor of one set of PAHs. The size difference was minimized by solvation of the less bulky PAH with methanol. Another set of PAHs showed an increase in separation with an increase in water

concentration. This was attributed to the phase changing from polymeric-like to monomeric-like in structure. An increase in temperature induced a decrease in the separation factor and shortened retention times.

Monomeric and polymeric ODS phases were also examined for comparison and to help elucidate the liquid crystal retention mechanism [21, 22]. A pair of PAHs, different in their planarity, were used to determine separation factors, which correlates with the planarity recognition capability. Polymeric phases have a greater capability to recognize molecular planarity in PAHs. The polymeric phase has less molecular freedom of alkyl chains, as seen by solid-state nuclear magnetic resonance spectroscopy (CP/MAS NMR). It was concluded that very ordered phases should have stronger molecular planarity recognition capability. Increasing the temperature induced a decrease in the planarity recognition capability of polymeric ODS phases. CP/MAS NMR studies showed that the polymeric ODS phase changed from solid-like to liquid-like structures with increasing temperature. It was concluded that there are some similarities among polymeric ODS phases and the liquid crystal phase in their planarity recognition capability. The liquid crystal phase is higher than the polymeric phase in planarity recognition because of its highly ordered and more rigid structure. Liquid crystalline phases have a higher degree of order

resulting from alignment of the rod-like substituent molecules. Low correlation was seen between the monomeric phase and the liquid crystal phase.

PAH separations by HPLC have been used in the previous studies mentioned here because much is known about the retention of these solutes on chemically bonded stationary phases. The retention mechanism is thought to be controlled by many factors. The molecular shape and size of the PAH is the primary factor influencing retention, although the π-electron interactions between the solute and the stationary phase also play an important role [23, 24].

Two parameters have been looked at for comparison of PAHs. The molecular size of PAHs has been represented by the F number proposed by Schabron, et al. [25], which is defined as F = (the number of double bonds) + (the number of primary or secondary carbons) - 0.5 x (the number of non-aromatic rings). The two dimensional shape of PAHs is generally represented by the length-to-breadth (L/B) ratio, which was proposed by Wise, et al. [26], and is defined by projecting the molecular dimensions on a flat surface. Therefore, L/B indicates two-dimensional molecular shape. These factors along with the hydrophobicity determine the retention of a particular solute [24].

Much has been learned from work done by Sander, et al. [21, 22, 27] about the effects of bonded phase length and

temperature on PAHs in reverse phase chromatography. The highest degree of shape recognition was achieved with long chain length alkyl phases. Column selectivity was found to vary continuously with temperature, regardless of the type of phase used. The selectivity factor for two PAHs, 1,2:3,4:5,6:7,8-tetrabenzonaphthalene (TBN) and benzo[a]pyrene (BaP), was examined and an empirical classification scheme was developed. Phases with selectivity $\geq$ 1.7 were described as "monomeric-like". Phases with selectivity < 1 were described as "polymeric-like". Phases with selectivity between these two classes were described as "intermediate". The temperature of analysis could convert one type of column into another. Polymeric phases were shown to give the best shape recognition ability of the columns tested. As a result of this, the Vydac C_{18} column (a polymeric column) was selected for comparison with the liquid crystal column.

The retention of planar and nonplanar PAHs has been described in terms of a schematic representation of molecular shape and bonded phase structure referred to as the "slot model" [28]. This model is not intended to describe the actual morphology of the bonded phase, but rather it is used to explain trends in retention that arise from differences in the molecular shape of the solute. Long narrow solutes can be retained longer in these slots than

bulkier solutes. The planarity of a solute also increases its respective retention time, owing to the fact that it fits into more "slots" and can interact more strongly with the bonded phase. Nonplanar solutes are more restricted from the slots than the corresponding planar solutes.

Studies have been performed comparing liquid crystals in GC to polymeric stationary phases in HPLC [14, 27]. It was concluded that there is less chain mobility as the temperature decreases. Bonded alkyl chains have been shown to straighten at reduced temperatures. This gives the polymeric stationary phase its liquid crystal-like retention properties. The polymeric column examined didn't exhibit a phase change in its Van't Hoff plot. This was attributed to the lack of mobility of the polymeric chains.

The objective of this work is to better understand the retention mechanism of PAHs in HPLC, utilizing both a liquid crystal material and a C_{18} material as stationary phases for the separation. The function of the liquid crystal stationary phase with respect to temperature is also reported in this paper. Three different organic solvents were used to test the effect of % organic on the retention and selectivity. Two groups of PAHs were used on the polymeric C_{18} bonded phase to determine differences in retention mechanisms.

EXPERIMENTAL

Reagents

The anthracene and phenanthrene used were of analytical-reagent grade, obtained from Sigma Chemicals (St. Louis, MO, USA). The mixture containing an acetonitrile solution of three polycyclic aromatic hydrocarbons (Standard Reference Material 869), benzo[a]pyrene (BaP), 1,2:3,4:5,6:7,8-tetrabenzonaphthalene (TBN), and phenanthro[3,4-c]phenanthrene (PhPh), was a gift from L. Sanders at the National Institute of Standards and Technology (Gaithersburg, Maryland, USA). Solvents in the HPLC experiments were of chromatographic grade, obtained from J.T. Baker Chemical Company (Phillipsburg, NJ, USA).

Columns

The column containing the liquid crystal stationary phase, 4-[4-(allyloxy)benzoyloxy]biphenyl, was prepared as described by Pesek, et al. [29]. The Vydac 201TP C_{18} was packed using a Hasken (Burbank, CA, USA) pneumatic amplification pump with methanol as the driving solvent with commercial C_{18} Vydac silica (a polymeric C_{18} column; The Separations Group, Hesperia, CA, USA). The column was 15 cm in length.

Apparatus

Column temperatures were regulated by means of a column heater, Pickering Laboratories, Model CHX 650 (Mountain View, CA, USA). The Dionex (Sunnyvale, CA, USA) HPLC system consisted of a GPM-2 Gradient Pump Module, a Dionex VDM-2 Variable Detector Module, an EDM-2 Eluant Degas Module, and a MIV Micro Injection Valve for manual injecting of the BaP, TBN, and PhPh mixture. A Spectra-Physics (San Jose, CA, USA) Model SP8875 autosampler was used for automatic injecting of the phenanthrene/anthracene mixture. A Dionex AI-450 Data system was used for data collecting.

Procedure

Several experiments were performed using either the Vydac 201TP C_{18} column or the liquid crystal column mentioned above. Both the liquid crystal column and the Vydac 201TP column were used for temperature studies. An isocratic mobile phase of 50% acetonitrile was used for the liquid crystal column. A flow rate of 1.0 ml/min was used at a wavelength of 254 nm. The temperature was varied from 25°C to 75°C, ±1°C, in 5°C increments, to observe the effect of temperature on the separation of anthracene and phenanthrene. The Vydac 201TP column was tested similarly, with a 50% acetonitrile mobile phase, flow of 1.0 ml/min, wavelength of 254 nm, and temperature varying from 25°C to

70°C, in 5°C increments. A temperature equilibration time of 20 minutes was used between runs and at every temperature, samples were run in duplicate.

The Vydac 201TP column was also tested from 25°C to 75°C and from 75°C to 25°C, in 10°C increments. All conditions were as mentioned above for testing the heating as well as cooling effects on the stationary phase.

Characterization of the retention mechanism of polynuclear aromatic hydrocarbons on a polymeric phase was performed on the Vydac 201TP C_{18} column. The three PAH test mixture obtained from NIST was eluted on the Vydac 201TP column using a 75% acetonitrile mobile phase, a flow rate of 1.0 ml/min, and a wavelength of 254 nm for detection. The temperature was again varied from 25°C to 70°C, in 5°C increments. A 20 minute equilibration time was allowed between temperatures. All temperature test points were done in duplicate. The liquid crystal column was also tested with this test mixture, but a steady baseline was not achieved with the 75% acetonitrile. Lower concentrations of organic solvent resulted in irregular peak shapes with very long retention times. The retention of these three PAHs could therefore not be evaluated on the liquid crystal stationary phase.

The Vydac 201TP column was also used for characterization of mobile phase effects on the retention of

PAHs. Methanol, acetonitrile, and tetrahydrofuran were individually varied from 25% to 90% organic. Anthracene and phenanthrene were used as test solutes for resolution, with a flow rate of 1.0 ml/min and a wavelength of 254 nm. A thirty minute equilibration time was allowed between different concentrations of mobile phase. Nitrate was injected on both columns to determine the void volume.

RESULTS AND DISCUSSION

Liquid Crystals as a Bonded Phase in PAH Separation

Fig. 1 is a diagram of the structure of the starting liquid crystal and the resultant silane reagent used to bond the material to porous silica. Both materials were characterized by diffuse reflectance infrared Fourier transform and carbon-13 cross-polarization magic angle spinning NMR spectra [29]. Carbon elemental analysis was used to verify a high amount of surface loading, with a surface coverage of 3.55 mmole/m^2.

Anthracene and phenanthrene were selected for separation on the liquid crystal stationary phase because much work has been done with these two polynuclear aromatic hydrocarbons. Their structures are depicted in Fig. 2. The molecular sizes of these two PAHs are the same (F = 7.0), but their shapes are different (anthracene's L/B = 1.57, phenanthrene's L/B = 1.46). As expected from the slot model [21], anthracene is retained longer that phenanthrene on the liquid crystal stationary phase at 50% acetonitrile, ambient temperature. Plots of log k' vs 1/T (Van't Hoff plot) are useful in determining if the solute interaction with the bonded phase has changed. A "break" in this type of plot is indicative of a phase transition.

Table 1 is a summary of the data over the specified temperature range. Fig. 3 is the Van't Hoff plot for phenanthrene and anthracene. Fig. 4 is a plot of the relative retention of anthracene and phenanthrene (k'_2/k'_1) vs. temperature. No distinct phase transition is observed in either plot.

Jinno, et al. [30] predicted in previous studies of PAHs that a critical change in selectivity would occur in a distinct transition. This would signal a change from a "solidlike" to a "liquidlike" behavior. Liquid crystals are known to exist in a rodlike alignment of substituent molecules. They are also known to undergo a transition from a type of material that is similar in properties to a solid to a type of material that is similar in properties to a liquid. The lack of a phase transition indicates that the transition temperature was not reached in this study.

It has been seen previously by Sander, et al. [22], that as temperature increases, the order of the bonded phase decreases for polymeric and monomeric C_{18} phases. It was also proposed that the chain mobility decreases with temperature. The liquid crystal bonded phase is known to become more rigid and rodlike at lower temperatures. The trend toward less discrimination between phenanthrene and anthracene at higher temperatures is observed from the data. This supports the theory that at higher temperatures, the

bonded phase becomes less ordered. The slot theory of rigid interaction sites existing on the bonded phase seems less likely at these higher temperatures.

As mentioned previously, anthracene and phenanthrene differ in their two-dimensional shape. In general, a high degree of shape recognition ability exists for phases with a high selectivity factor (k'_{anth}/k'_{phen}). Anthracene has a larger L/B ratio than phenanthrene, allowing for discrimination in the separation by the slot model theory. As the temperature increases, the ability to discriminate shape becomes less and less. This is expected if the bonded phase is becoming less rigid in structure.

Previous work done by Pesek, et al. [17] with a similar liquid crystal stationary phase, [4-(allyloxy)benzoyloxy]-4-methoxyphenyl (ABMP), shows comparable results. The selectivity factor at 25°C for ABMP (1.29) is very close to that achieved in this study (1.27). It should be noted that the mobile phase composition is slightly different (30:70) from what we used (50:50). Pesek found previously that as the amount of water is increased, the liquid crystal mobile phase should become more ordered and aggregate in more of a slot-like structure. Similar results are expected with the liquid crystal stationary phase studied here.

One of the goals of this project was to synthesize a stable liquid crystal stationary phase that displays

variable selectivity with respect to molecular shape as a result of temperature or solvent conditions. The k' values didn't abruptly change during the course of our experiment. This would indicate that the phase is stable and that the liquid crystal wasn't irreversibly changed during the course of the experiment. Further studies of this stationary phase at San Jose State demonstrate results consistent with initial data obtained on this column.

Vydac 201TP as a Bonded Phase in PAH Separation

The Vydac 201TP stationary phase is a polymeric material used routinely in the separation of polynuclear aromatic hydrocarbons. Anthracene and phenanthrene were again used for testing of temperature effects on this column. Table 2 is a summary of the temperature test points for the Vydac column. Fig. 5 is the Van't Hoff plot for this data. As can be seen from this plot, no phase transition appears to be taking place. This is to be expected for a polymeric phase if it is assumed that the alkyl chain association does not change abruptly with temperature.

Previously, Sander, et al. [22] found similar results with the same type of phase. The monomeric phase tested did exhibit a phase change transition between 40°C and 50°C. As suggested previously, this implies that the polymeric phase has constraints on its chain mobility that the monomeric phase doesn't. The monomeric phase must become less ordered and less rigid in structure as it is heated.

The proposed slot model that depicts the order of the bonded phase layer as a series of slots again explains the results seen here. The polymeric phase consists of an ordered structure that has little freedom for chain mobility. Temperature has a gradual effect on this mobility, as can be seen from the smooth Van't Hoff plot.

Fig. 6 is a selectivity plot of anthracene and phenanthrene as a function of temperature for the Vydac 201TP column. As can be seen from the data, temperature can be used to manipulate separations. The smooth separation curve can be explained in terms of the chain mobility of the stationary phase. Previous work has been done in which bonded ligand mobility is observed by NMR [31] and by inelastic neutron scattering [32] as a function of temperature. The mobility of the alkyl chains decreases with temperature. The alkyl bonded phase becomes more rodlike and rigid at lower temperatures. The Vydac 201TP polymeric phase has been compared previously to a liquid crystal in PAH separation characteristics [22].

The prediction of a distinct phase transition by Jinno, et al. [30], previously discussed, does not correlate with the data found here. A gradual change in shape selectivity over the temperature range tested here is what is observed in Fig. 6.

A comparison can be made between Fig. 4 and Fig. 6, selectivity vs temperature on the liquid crystal column and the selectivity vs temperature on the Vydac 201TP C_{18} column (Fig. 7). The liquid crystal bonded phase appears to undergo much smaller changes than the Vydac 201TP column. This can be attributed to the high selectivity the liquid crystal column has for shape recognition. Anthracene's two

dimensional shape is longer and narrower than phenanthrene (L/B of anthracene=1.57, L/B of phenanthrene=1.46). Even at elevated temperatures, the liquid crystal column can selectively retain different shape species, with a moderate decrease in the selectivity factor. At elevated temperatures, the Vydac 201TP column approaches a selectivity factor of 1.0.

It can be concluded that the Vydac 201TP stationary phase is becoming less ordered with an increase in temperature. As such, its ability to discriminate based on shape of solute molecules decreases considerably. The rigid structure of alkyl chains at lower temperatures becomes relaxed as the phase is heated. The liquid crystal stationary phase does demonstrate a decrease in selectivity with an increase in temperature, but the changes are small over the range studied. The liquid crystal stationary phase must be less disrupted by heating than the Vydac 201TP. The slot theory becomes less prominent at elevated temperatures, but the liquid crystal moiety retains some of its shape selectivity characteristics. This may be due to a disruption of the "slot" so that different shapes fit in with less discrimination, or another structure occurs with the absence of slots in the bonded phase.

Further studies in the area of liquid crystal stationary phases would help to elucidate possible solute -

bonded phase interactions. Specific polynuclear aromatic hydrocarbons could be used that have different L/B measurements. The shape and size of the slot could be understood by determining which PAHs could be retained longest by the stationary phase. Temperature could also be increased even further than in this study to determine if the shape selectivity of the liquid crystal greatly diminishes at a certain point or if it continues to be a gradual change. This of course depends on the composition of the mobile phase which determines the upper temperature limit.

Table 3 contains data from the Vydac 201TP column with anthracene and phenanthrene. Temperature test points were taken in both the heating and cooling directions. The results of this experiment will determine whether there is any change in selectivity during the two processes. As can be seen from Fig. 8, the heating and cooling effects are similar on the Van't Hoff plot. Fig. 9 shows the consistent behavior of the stationary phase in either direction as well. From these data, it can be concluded that the ordering of the Vydac 201TP phase is temperature dependent and completely reversible under the conditions studied.

The liquid crystal stationary phase is currently being tested in the forward and reverse directions of temperature. Preliminary results demonstrate that retention in the

heating cycle is greater than in the cooling cycle (Fig. 10). These results indicate that the liquid crystal in HPLC is not always reversible after heating and cooling cycles. Many of the liquid crystal stationary phases used previously were unstable at higher temperatures [7,10]. Previous work with liquid crystals in gas chromatography has demonstrated reversibility of the stationary phase over typical heating and cooling temperature ranges.

Vydac 201TP as a Bonded Phase for Separation of a Column Selectivity Test Mixture

A test mixture designed for the evaluation of C_{18} columns has been developed by a group at NIST (National Institute of Standards and Technology) [33]. An empirical test has been derived that classifies C_{18} columns into one of three groups, based on retention behavior. The test mixture consists of three PAHs, benzo[a]pyrene (BaP), tetrabenzonaphthalene (TBN), and phenanthro[3,4-c]phenanthrene (PhPh). The quantitative measure of phase selectivity toward PAHs is given by the selectivity coefficient $\alpha_{TBN/BaP}$. As can be seen in Fig. 11, the relative planarities of BaP and TBN are different, BaP being planar, TBN being non-planar. The classification scheme for column selectivity toward different PAHs is the following: a) $\alpha_{TBN/BaP} < 1$ "polymeric-like", b) $1 < \alpha_{TBN/BaP} < 1.7$ "intermediate", c) $1.7 \leq \alpha_{TBN/BaP}$ "monomeric-like".

The Vydac 201TP column was selected for testing with this test mixture because it has shown polymeric-like behavior in previous studies [22, 33]. This type of behavior has been found to be comparable with liquid crystalline phases in GC [27]. The retention mechanism of this polymeric phase should therefore be similar to the mechanism occurring with the liquid crystalline phase tested here.

Table 4 is a summary of the data collected using the Vydac 201TP column and the three PAH mixture. Fig. 12 is the Van't Hoff plot of the data for each of the three components. As was seen with the anthracene and phenanthrene data, no phase transition is obvious with the nonplanar PAHs. BaP, at lower temperatures, exhibits a slow change in retention, due to its planarity. This would again suggest that the polymeric phase has constraints with regard to the alkyl chains present on the surface. A deviation in linear behavior is observed with BaP. The retention mechanism of the other two PAHs must be different than that of the BaP. No abrupt change is detected over the temperature range. The conformation of the planar PAH (BaP) is unaffected by temperature changes, indicating that the selectivity changes are a function of the bonded phase. The plots of PhPh and TBN are similar in characteristics to the Van't Hoff plots of anthracene and phenanthrene (Fig. 5).

In a similar experiment carried out by Sander, et al. [22], the same selectivity mixture was used. The Vydac 201TP column was tested, as well as two other C_{18} columns. The data from Sander's study was used to establish the classification scheme of "momomeric-like" and "polymeric-like". The Van't Hoff plots in Fig. 12 are in agreement with Sander's observations.

Fig. 13 is a selectivity plot of PhPh, TBN, and BaP vs temperature. The plot displays a region where the bonded phase exhibits polymeric type behavior. At about 50°C, coelution of TBN and BaP is seen. At this elevated temperature, the bonded phase becomes less restricted and therefore loses some of its shape recognition ability.

The selectivity of the stationary phase for PhPh and TBN slightly decreases over the entire temperature range tested here. The change is very small, indicating that the selectivity of PhPh and TBN is not affected by temperature. This is to be expected, in that both solutes are nonplanar. The separation factor of PhPh and BaP increases with respect to temperature, until a temperature of 50°C is reached. At that point, the selectivity factor levels off for the rest of the temperature range. This behavior is similar to the selectivity between TBN and BaP. Looking again at the Van't Hoff plots, this divergence in behavior of BaP with respect to PhPh and TBN can be seen at about 50°C as well. The retention mechanism of BaP must therefore be different from that of PhPh and TBN. The planarity factor difference between BaP and the other two PAHs is most likely the cause for this retention variation, although differences in size may also have an effect on selectivity. Above 45°C, the stationary phase becomes less ordered. The "slots" that make up the bonded phase become less restrictive of

nonplanar solutes. The change in the stationary phase selectivity suggests that a minor phase transition may be occurring over the temperature range studied.

In the work by Sander, et al. [22] (see above), similar experiments showed different results with respect to selectivity. A change in the order of elution was seen by Sander for the three PAHs tested. At about 35°C, TBN and BaP coeluted. BaP was then separated from TBN at about 40°C, eluting second in order. Fig. 14 is an overlay of the chromatograms reported here for different temperature test points. In these chromatograms, no inversion of elution order is seen.

The selectivity difference we observed below 50°C for BaP, with respect to PhPh and TBN, was also not seen by Sander. The Vydac 201TP stationary phase he used showed a linear response for selectivity over the temperature range studied here. This suggests that there are differences in batch to batch lots of the Vydac 201TP stationary phase that could lead to differences in retention behavior.

The "slot model" explains the differences in retention of planar versus nonplanar solutes. Experiments reported, though, demonstrate a dependence of retention on temperature for planar molecules. A change in the ordered phase that accounts for interaction differences may be occurring. The polymeric phase tested here did exhibit both "polymeric" and

"intermediate" selectivity, as defined by Sander. The temperature range where the transition occurred was between 45°C and 50°C. Sander found a similar temperature transition between 40°C and 45°C. This difference could again be explained by variations in the bonded phase, the phase used in Sander's study exhibiting less polymeric behavior.

The liquid crystal stationary phase column was also used for testing with the column selectivity test mixture. Problems were seen with the mobile phase required for elution of the three components. A 75% acetonitrile mobile phase was needed for elution of the PAHs. The baseline was unstable at this concentration of organic solvent, making accurate data collection impossible.

The Effects of Organic Modifier on the Vydac 201TP Stationary Phase Separation of Two PAHs

The organic modifier and percent of organic in a mobile phase can have a big effect on the selectivity and retention of solutes. The full characterization of a stationary phase is not complete without information regarding mobile phase effects of a separation. The Vydac 201TP stationary phase has been characterized in depth using acetonitrile as the organic solvent. In our work described above, we used acetonitrile as the modifier, the percent of which was determined by previous work of other researchers. This allowed direct correlation between experimenters.

Three common organic modifiers used often in HPLC are acetonitrile, methanol, and tetrahydrofuran. Various percents of these have been used, depending on the particular application. Recent work done by Pesek, et al. [17] reports effects of mobile phase composition on a liquid crystal stationary phase. This liquid crystal stationary phase, [4-(allyloxy)benzoyloxy]-4-methoxyphenyl (ABMP), is similar in structure to that used in the studies reported here. Similar tests have not been reported for the Vydac 201TP stationary phase.

Tables 5, 6, and 7 are a summary of the results found with the Vydac 201TP stationary phase and varying acetonitrile, methanol, and tetrahydrofuran mobile phase

compositions, using phenanthrene and anthracene for characterization. Figs. 15 and 16 are plots of Log K' vs % organic solvent for both phenanthrene and anthracene.

Lochmuller, et al. [19] proposed that in the presence of a hostile solvent, bonded phases collapse to minimize the surface area in contact with the solvent molecules. The hostile or polar solvent induces a conformational change of the silane ligands. Polymeric phase collapse appears to be different from monomeric phase collapse, due to the fact that polymeric phases appear to have more constraints on their structure. A polymeric phase was compared to a sponge, in that it swells in a non-polar solvent and shrinks in a polar solvent.

Looking at Figs. 15 and 16, it can be seen that the no distinct point of collapse is seen. Pesek, et al. [17] found that for the liquid crystal stationary phase tested in their experiments, a specific point of collapse was seen for each solvent tested. Therefore, a distinct point of change does not exist where the Vydac 201TP stationary phase changes conformation, dependent on the polarity of the mobile phase used. This would indicate that a more ordered structure exists for the liquid crystal stationary phase than the polymeric stationary phase. A slow conformational change may be occurring that is a function of the solvent polarity. The stationary phase does retain anthracene and

phenanthrene, dependent on the polarity of the solvent. The solvents used, listed in sequence from most polar to least polar, were methanol, acetonitrile, and tetrahydrofuran. The more polar the mobile phase, the longer the analytes are retained.

Previously, a theory of silanophilic as well as solvophobic interaction with the stationary phase has been postulated [18, 34]. In this theory, hydrophobic interactions occur, in addition to binding with accessible silanol groups. Retention consists of two factors, silanophilic being predominant at high % organic solvents. A minimum in the plot of retention versus % organic is seen when the sum of both factors is at a minimum.

Our results do not support this theory, in that no minimum is observed for the retention versus organic composition of the solvent. Slight curvature is seen in the plots, indicating greater retention at low water concentrations than expected from retention observed at high water concentration , assuming regular reverse behavior (linear relationship between logarithmic retention factor and solvent composition). This may indicate that the silanophilic interactions, though slight, are actually occurring, resulting in a small effect in the overall retention.

Fig. 17 consists of the anthracene and phenanthrene selectivity plots for each organic modifier. The selectivity of all three organic modifiers can be seen to be linear with relatively small changes occurring over the modifier concentration range. As the polarity of the solvent increases, an increase in the selectivity is seen. This supports the previously postulated theory of collapse occurring with more hostile solvents. This collapse or change in conformation of the stationary phase then leads to a more ordered bonded phase. The closer proximity of the bonded moieties allows for greater selectivity.

CONCLUSIONS

Polynuclear aromatic hydrocarbons are useful in testing the interactions of solutes with new types of stationary phases. A liquid crystal stationary phase column was prepared using 4-[4-(allyloxy)benzoyloxy]biphenyl as the bonded moiety. Anthracene and phenanthrene were used to determine selectivity and retention of this stationary phase. No distinct phase transition is observed when the data is analyzed by a Van't Hoff plot of log k' vs 1/T. The plot of relative retention of anthracene and phenanthrene as a function of temperature shows that the transition may be a gradual one occurring over the temperature range studied. The temperature range tested did not contain the phase transition temperature of the liquid crystal bonded phase.

Previous data from Sander, et al. [22] suggested that the order of a polymeric bonded phase decreases as temperature increases. Liquid crystals are known to become more rigid and rodlike at lower temperatures, behaving "polymeric-like". Less discrimination between the two PAHs is seen at higher temperatures, as was seen with polymeric phases tested previously. The slot theory of retention that describes the solute interaction with the stationary phase is supported by the work done in this study. Anthracene, the longer of the PAHs studied here, is selectively retained

on the liquid crystal phase more than phenanthrene. This selectivity is decreased with increasing temperature.

Our results resemble previous work done with other liquid crystal stationary phases [17]. The stability of the column is demonstrated by the fact that no reversible degradation of the column occurred with changing temperature. The k' values didn't change abruptly during the course of the experiment, also demonstrating a stable bonded phase.

Similar studies to those done with the liquid crystal were performed on a polymeric Vydac 201TP column. No phase transition occurred over the temperature range studied. This type of result had been found by Sander, et al. [22] with the same type of phase. The rigidity of the polymeric chain explains the consistent behavior of the column over the temperature range studied here. Testing of the Vydac stationary phase in both the heating and cooling directions demonstrated that the processes are identical with respect to anthracene and phenanthrene retention. Retention in the heating cycle is greater than in the cooling cycle for the liquid crystal stationary phase.

The changes in the Vydac 201TP column with temperature are greater than those for the liquid crystal column. The liquid crystal column undergoes smaller changes in selectivity than does the Vydac 201TP column. The liquid

crystal stationary phase may be undergoing a relaxed "slot" formation that still retains some of its shape recognition ability.

Another type of test mixture for characterization of stationary phases has been developed by a group at NIST [33]. This mixture contains 3 PAHs that vary in their deviations from planarity. The slot theory, based on shape selectivity retention, can be tested for a particular stationary phase. The liquid crystal stationary phase was tested using this mixture, but problems with a stable baseline were seen with the high organic solvent needed for elution (75% acetonitrile). Using this mixture, Sander tested the Vydac 201TP C_{18} column over a wide temperature range [22]. Our results confirmed the lack of a phase transition with temperature, although a minor change may be occurring with the stationary phase between 45°C and 50°C that can slightly affect selectivity.

The stationary phase exhibited "polymeric-like" and "intermediate-like" behavior, based on the selectivity factor of two of the PAHs. Analyzing the selectivity data, a difference can be seen between the two nonplanar PAHs and the planar one. The slot mechanism of retention, in which planar solutes are preferentially retained over nonplanar solutes, explains this phenomenon. Differences in data from our results and those of Sander can be explained by slight

differences in stationary phases and effective column length.

Mobile phase effects were also tested using the Vydac 201TP column. Similar tests have been previously performed on a liquid crystal column [17]. The polymeric phase we tested didn't exhibit a point of collapse, where the stationary phase minimizes contact with the solvent molecules. The liquid crystal column previously tested demonstrated a similar type of behavior. The polarity of the solvent did have an effect on the retention of anthracene and phenanthrene. The more polar the mobile phase, the longer the analytes are retained. Selectivity data suggests that a gradual change may occur in the stationary phase. A slow collapse may be occurring as the mobile phase becomes more polar.

The theory of silanophilic interactions occurring in which the solute molecules are secondarily retained by silanol groups is not supported from the data found here. A minimum in the retention data versus amount of organic solvent would indicate silanophilic interactions. There does appear to be greater retention than expected from only solvophobic interactions, suggesting that perhaps silanophilic interactions are occurring, but to a much lesser extent than the hydrophobic ones.

Future studies in the area of more varied solutes might elucidate the actual structure of the bonded moiety. Various lengths of PAHs could be used to identify specific "slot" sizes and points of interaction. Liquid crystal columns will also be useful, in that they have ordered phases similar to polymeric C_{18} phases, but they undergo distinct transitions, similar to monomeric C_{18} phases. Mobile phase composition can be varied to optimize selectivity and retention, with temperature adjustments allowing a "polymeric-like" column to behave in a "monomeric-like" fashion.

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TABLE 1

SELECTIVITY AND RETENTION OF PHENANTHRENE AND ANTHRACENE ON A LIQUID CRYSTAL STATIONARY PHASE

Temp °C	Phen Vol	K'1	Log K'1	Anth Vol	K'2	Log K'2	α K'2/K'1
25	14.15	6.99	0.845	17.53	8.90	0.950	1.27
25	14.15	6.99	0.845	17.52	8.90	0.949	1.27
30	13.60	6.68	0.825	16.77	8.47	0.928	1.27
30	13.60	6.68	0.825	16.77	8.47	0.928	1.27
35	13.07	6.38	0.805	15.98	8.03	0.905	1.26
35	13.08	6.39	0.805	16.03	8.06	0.906	1.26
40	12.65	6.23	0.794	15.45	7.83	0.894	1.26
40	12.65	6.23	0.794	15.45	7.83	0.894	1.26
45	12.25	6.00	0.778	14.95	7.54	0.878	1.26
45	12.27	6.01	0.779	14.88	7.50	0.875	1.25
50	11.87	5.78	0.762	14.38	7.22	0.858	1.25
50	11.87	5.78	0.762	14.35	7.20	0.857	1.25
55	11.52	5.66	0.753	13.90	7.03	0.847	1.24
55	11.47	5.63	0.751	13.82	6.99	0.844	1.24
60	11.05	5.39	0.731	13.28	6.68	0.825	1.24
60	11.03	5.38	0.730	13.27	6.67	0.824	1.24
65	10.68	5.21	0.717	12.77	6.42	0.808	1.23
65	10.68	5.21	0.717	12.80	6.44	0.809	1.24
70	10.33	5.01	0.699	12.28	6.14	0.788	1.23
70	10.33	5.01	0.699	12.35	6.18	0.791	1.23
75	9.98	4.80	0.681	11.83	5.88	0.769	1.22
75	10.00	4.81	0.683	11.80	5.86	0.768	1.22

TABLE 2

SELECTIVITY AND RETENTION OF PHENANTHRENE AND ANTHRACENE ON A VYDAC 201TP STATIONARY PHASE

Temp °C	Phen Vol	K'1	Log K'1	Anth Vol	K'2	Log K'2	α K'2/K'1
25	12.47	6.17	0.790	15.30	7.79	0.892	1.26
25	12.47	6.17	0.790	15.30	7.79	0.892	1.26
30	11.62	5.68	0.754	14.02	7.06	0.849	1.24
30	11.60	5.67	0.753	14.00	7.05	0.848	1.24
35	10.88	5.25	0.720	12.97	6.45	0.810	1.23
35	10.87	5.25	0.720	12.95	6.44	0.809	1.23
40	10.23	4.88	0.688	12.05	5.93	0.773	1.21
40	10.23	4.88	0.688	12.05	5.93	0.773	1.21
45	9.67	4.56	0.659	11.25	5.47	0.738	1.20
45	9.68	4.56	0.659	11.25	5.47	0.738	1.20
50	9.13	4.25	0.628	10.57	5.07	0.705	1.19
50	9.13	4.25	0.628	10.53	5.05	0.703	1.19
55	8.68	3.99	0.601	9.95	4.72	0.674	1.18
55	8.68	3.99	0.601	9.95	4.72	0.674	1.18
60	8.23	3.73	0.572	9.35	4.37	0.641	1.17
60	8.23	3.73	0.572	9.37	4.39	0.642	1.18
65	7.80	3.48	0.542	8.82	4.07	0.609	1.17
65	7.80	3.48	0.542	8.83	4.07	0.610	1.17
70	7.55	3.34	0.524	8.50	3.89	0.589	1.16
70	7.53	3.33	0.522	8.48	3.87	0.588	1.16

TABLE 3

SELECTIVITY AND RETENTION OF PHENANTHRENE AND ANTHRACENE ON A VYDAC 201TP STATIONARY PHASE, HEATING AND COOLING

Temp °C	Phen Vol	K'1	Log K'1	Anth Vol	K'2	Log K'2	α K'2/K'1
25	10.95	5.64	0.751	13.60	7.24	0.860	1.28
25	11.02	5.68	0.754	13.60	7.24	0.860	1.28
35	9.58	4.81	0.682	11.50	5.97	0.776	1.24
35	9.57	4.80	0.681	11.50	5.97	0.776	1.24
45	8.50	4.15	0.618	10.00	5.06	0.704	1.22
45	8.50	4.15	0.618	10.00	5.06	0.704	1.22
55	7.62	3.62	0.558	8.82	4.35	0.638	1.20
55	7.62	3.62	0.558	8.82	4.35	0.638	1.20
65	6.87	3.16	0.500	7.85	3.76	0.575	1.19
65	6.87	3.16	0.500	7.87	3.77	0.576	1.19
75	6.27	2.80	0.447	7.08	3.29	0.517	1.18
75	6.27	2.80	0.447	7.08	3.29	0.517	1.18
65	6.97	3.22	0.508	8.00	3.85	0.585	1.19
65	6.93	3.20	0.505	7.93	3.81	0.580	1.19
55	7.65	3.64	0.561	8.88	4.38	0.642	1.21
55	7.67	3.65	0.562	8.88	4.38	0.642	1.20
45	8.58	4.20	0.623	10.10	5.12	0.709	1.22
45	8.58	4.20	0.623	10.10	5.12	0.709	1.22
35	9.70	4.88	0.688	11.70	6.09	0.785	1.25
35	9.72	4.89	0.689	11.72	6.10	0.786	1.25
25	11.02	5.68	0.754	13.65	7.27	0.862	1.28
25	11.03	5.68	0.755	13.67	7.28	0.862	1.28

TABLE 4

SELECTIVITY AND RETENTION OF PhPh, TBN, AND BaP ON A VYDAC 201TP STATIONARY PHASE

Temp °C	PhPh Vol	K'1	Log K'1	TBN Vol	K'2	Log K'2
25	8.62	2.58	0.411	11.07	3.59	0.556
25	8.60	2.57	0.410	11.03	3.58	0.553
30	7.65	2.17	0.337	9.92	3.12	0.494
30	7.63	2.17	0.336	9.88	3.10	0.491
35	7.00	1.90	0.280	9.08	2.77	0.442
35	7.00	1.90	0.280	9.08	2.77	0.442
40	6.45	1.68	0.224	8.35	2.46	0.392
40	6.43	1.67	0.222	8.32	2.45	0.390
45	5.97	1.48	0.169	7.67	2.18	0.339
45	5.97	1.48	0.169	7.65	2.17	0.337
50	5.62	1.33	0.124	7.17	1.98	0.296
50	5.62	1.33	0.124	7.17	1.98	0.296
55	5.28	1.19	0.076	6.65	1.76	0.245
55	5.27	1.19	0.074	6.65	1.76	0.245
60	4.98	1.07	0.028	6.20	1.57	0.197
60	4.98	1.07	0.028	6.20	1.57	0.197
65	4.73	0.96	-0.017	5.85	1.43	0.155
65	4.70	0.95	-0.022	5.82	1.41	0.151
70	4.50	0.87	-0.062	5.50	1.28	0.108
70	4.50	0.87	-0.062	5.50	1.28	0.108

TABLE 4

(CONTINUED)

Temp °C	BaP Vol	K'3	Log K'3	α K'2/K'3	α K'1/K'2	α K'1/K'3
25	14.73	5.11	0.709	0.70	0.72	0.50
25	14.68	5.09	0.707	0.70	0.72	0.50
30	11.98	3.97	0.599	0.78	0.70	0.55
30	11.97	3.97	0.598	0.78	0.70	0.55
35	10.38	3.31	0.519	0.84	0.69	0.58
35	10.38	3.31	0.519	0.84	0.69	0.58
40	9.08	2.77	0.442	0.89	0.68	0.61
40	9.07	2.76	0.441	0.89	0.68	0.60
45	8.24	2.42	0.384	0.90	0.68	0.61
45	8.27	2.43	0.386	0.89	0.68	0.61
50	7.17	1.98	0.296	1.00	0.67	0.67
50	7.17	1.98	0.296	1.00	0.67	0.67
55	6.65	1.76	0.245	1.00	0.68	0.68
55	6.67	1.77	0.247	1.00	0.67	0.67
60	6.20	1.57	0.197	1.00	0.68	0.68
60	6.20	1.57	0.197	1.00	0.68	0.68
65	5.85	1.43	0.155	1.00	0.67	0.67
65	5.82	1.41	0.151	1.00	0.67	0.67
70	5.50	1.28	0.108	1.00	0.68	0.68
70	5.50	1.28	0.108	1.00	0.68	0.68

TABLE 5

SELECTIVITY AND RETENTION OF PHENANTHRENE AND ANTHRACENE, VARYING THE ACETONITRILE CONCENTRATION OF THE MOBILE PHASE

% ACN	Phen Vol	K'1	Log K'1	Anth Vol	K'2	Log K'2	α K'2/K'1
45	15.73	12.33	1.091	19.63	15.64	1.194	1.27
	15.52	11.93	1.077	19.30	15.08	1.178	1.26
50	9.92	7.27	0.861	12.02	9.02	0.955	1.24
	9.88	7.23	0.859	11.98	8.98	0.953	1.24
55	7.27	5.06	0.704	8.63	6.19	0.792	1.22
	7.27	5.06	0.704	8.63	6.19	0.792	1.22
60	5.37	3.48	0.541	6.22	4.18	0.622	1.20
	5.37	3.48	0.541	6.22	4.18	0.622	1.20
65	4.40	2.61	0.416	5.02	3.11	0.493	1.19
	4.42	2.62	0.419	5.02	3.11	0.493	1.19
70	3.63	1.98	0.296	4.07	2.34	0.368	1.18
	3.63	1.98	0.296	4.07	2.34	0.368	1.18
75	3.22	1.62	0.209	3.55	1.89	0.276	1.17
	3.25	1.64	0.215	3.60	1.93	0.285	1.17
80	2.87	1.33	0.125	3.12	1.54	0.187	1.15
	2.87	1.33	0.125	3.12	1.54	0.187	1.15
85	2.63	1.10	0.043	2.83	1.26	0.102	1.14
	2.63	1.10	0.043	2.83	1.26	0.102	1.14

TABLE 6

SELECTIVITY AND RETENTION OF PHENANTHRENE AND ANTHRACENE, VARYING THE METHANOL CONCENTRATION OF THE MOBILE PHASE

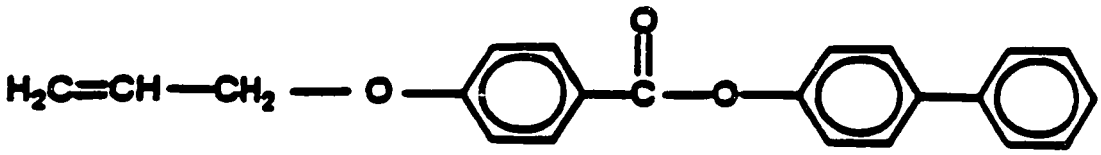
% MeOH	Phen Vol	K'1	Log K'1	Anth Vol	K'2	Log K'2	α K'2/K'1
60	18.50	14.68	1.167	25.10	20.27	1.307	1.38
60	18.62	14.78	1.170	25.25	20.40	1.310	1.38
65	12.65	9.54	0.980	16.98	13.15	1.119	1.38
65	12.63	9.70	0.987	17.00	13.41	1.127	1.38
70	7.87	5.67	0.754	10.17	7.62	0.882	1.34
70	7.88	5.57	0.746	10.17	7.48	0.874	1.34
75	5.65	3.63	0.560	7.07	4.80	0.681	1.32
75	5.65	3.63	0.560	7.08	4.80	0.682	1.32
80	4.07	2.31	0.363	4.85	2.94	0.469	1.27
80	4.08	2.32	0.365	4.88	2.97	0.472	1.28
85	3.32	1.66	0.219	3.82	2.06	0.313	1.24
85	3.30	1.64	0.215	3.82	2.06	0.313	1.25

TABLE 7

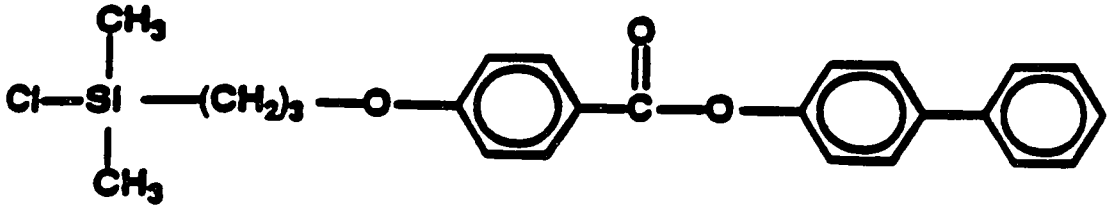
SELECTIVITY AND RETENTION OF PHENANTHRENE AND ANTHRACENE, VARYING THE THF CONCENTRATION OF THE MOBILE PHASE

% THF	Phen Vol	K'1	Log K'1	Anth Vol	K'2	Log K'2	α K'2/K'1
30	34.53	16.62	1.221	41.60	20.22	1.306	1.22
30	34.80	16.76	1.224	41.87	20.36	1.309	1.22
35	14.05	6.17	0.790	16.10	7.21	0.858	1.17
35	14.00	6.14	0.788	16.15	7.24	0.860	1.18
40	8.03	3.10	0.491	8.97	3.58	0.553	1.15
40	8.05	3.11	0.492	8.95	3.57	0.552	1.15
45	5.05	1.58	0.198	5.47	1.79	0.253	1.14
45	5.03	1.57	0.195	5.43	1.77	0.248	1.13
50	3.62	0.85	-0.072	3.80	0.94	-0.027	1.11
50	3.62	0.85	-0.072	3.80	0.94	-0.027	1.11

FIGURE 1

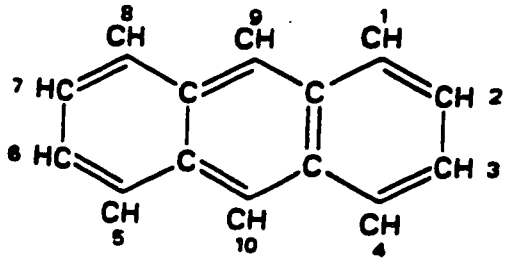


A. 4-[4-(ALLYLOXY)BENZOYLOXY]BIPHENYL

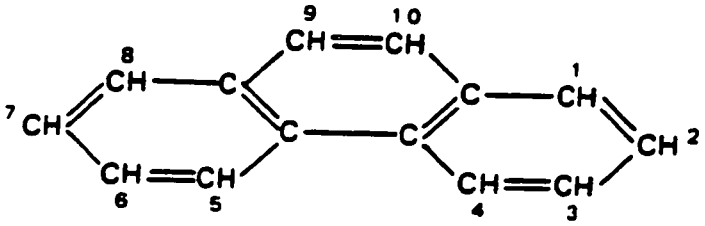


B. {[4-(3-CHLORODIMETHYLSILYL)PROPYLOXY]BENZOYLOXY}BIPHENYL

FIGURE 2



ANTHRACENE



PHENANTHRENE

FIGURE 3

RETENTION OF ANTHRACENE AND PHENANTHRENE ON A LIQUID CRYSTAL STATIONARY PHASE

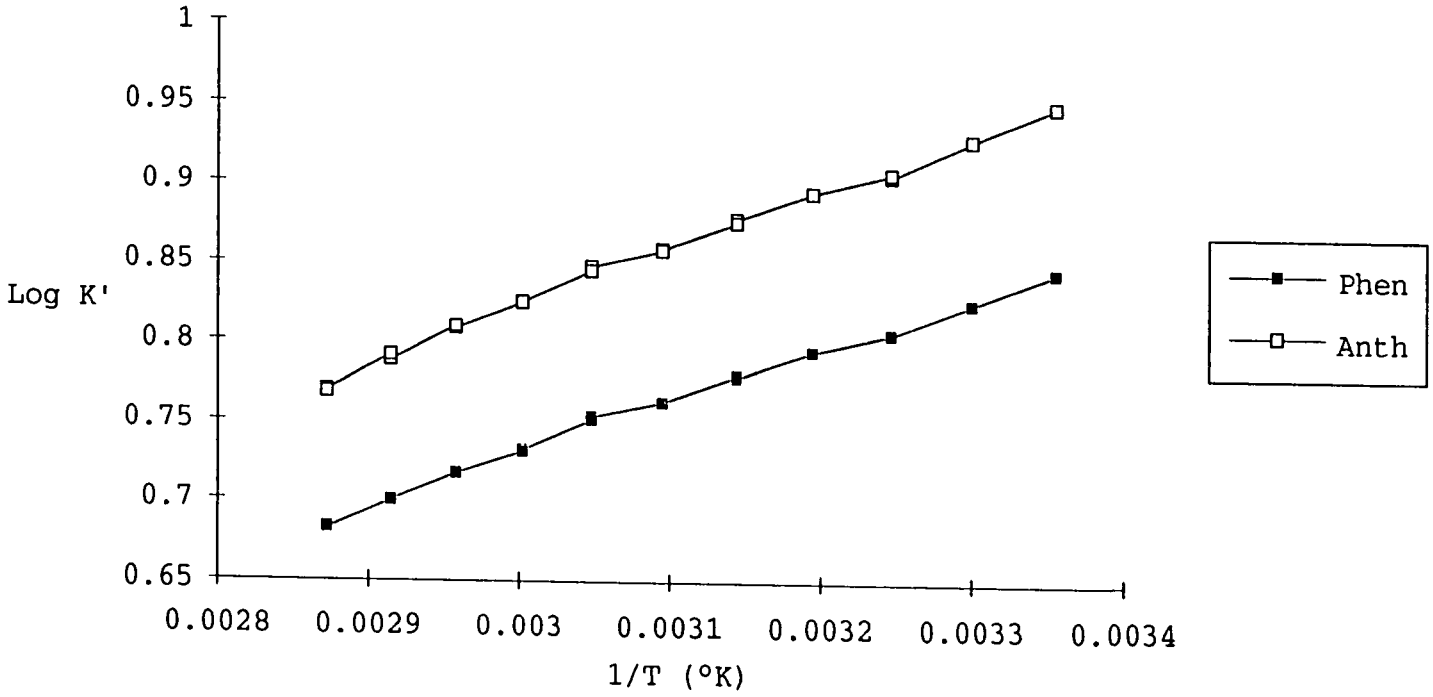


FIGURE 4

SELECTIVITY OF ANTHRACENE AND PHENANTHRENE ON A LIQUID CRYSTAL STATIONARY PHASE

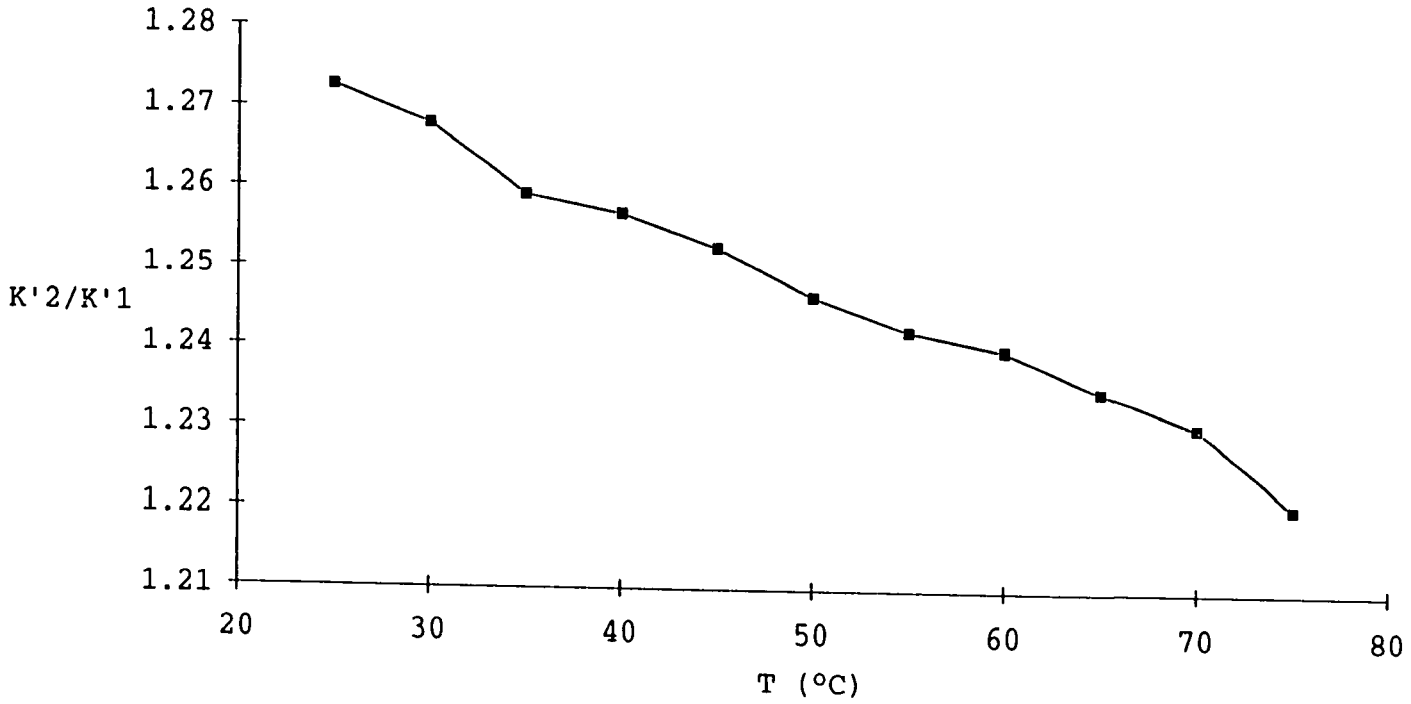


FIGURE 5

RETENTION OF ANTHRACENE AND PHENANTHRENE ON A VYDAC 201TP STATIONARY PHASE

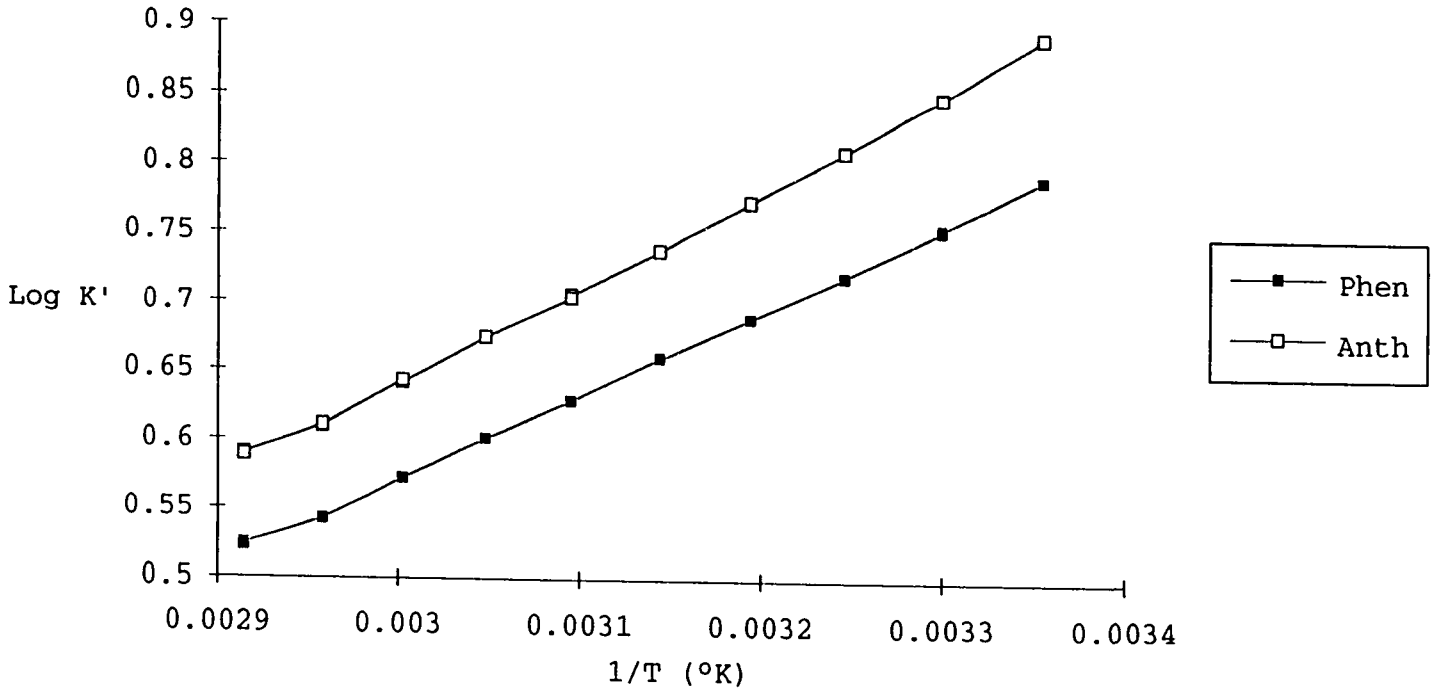


FIGURE 6

SELECTIVITY OF ANTHRACENE AND PHENANTHRENE ON A VYDAC 201TP STATIONARY PHASE

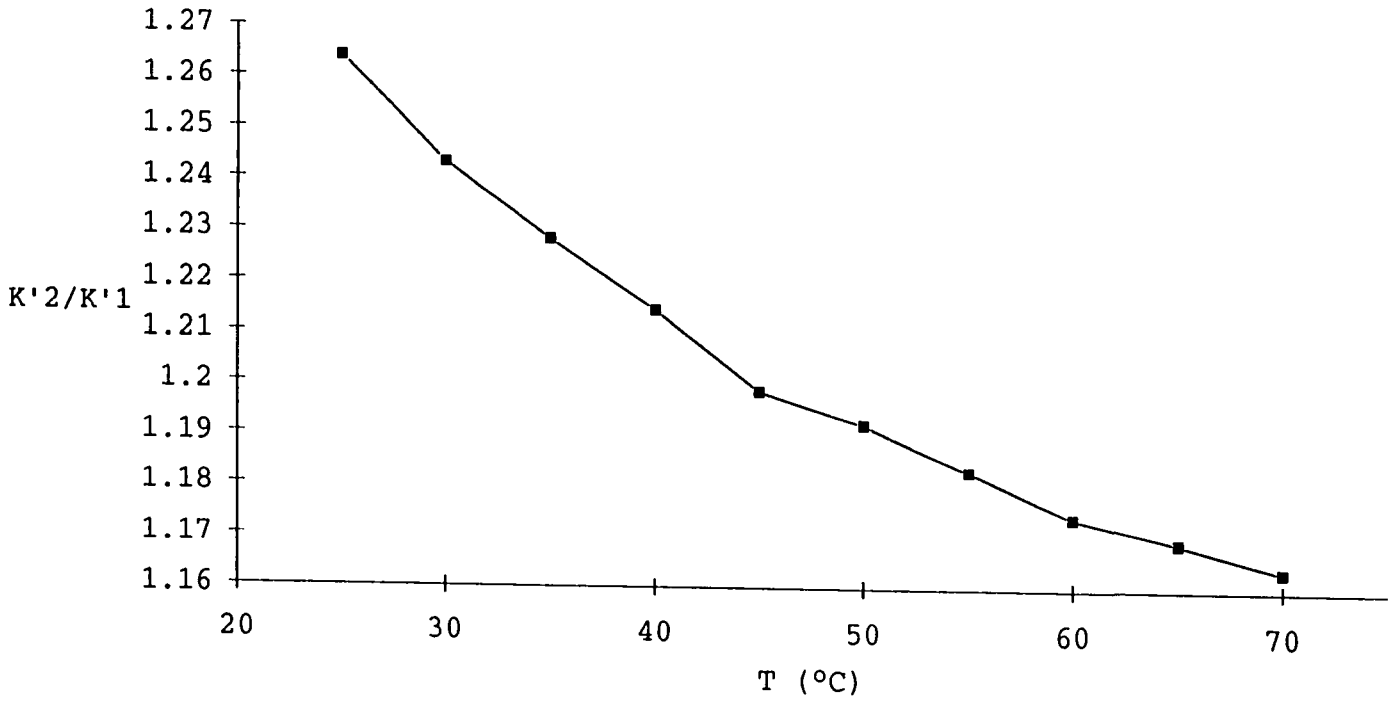


FIGURE 7

SELECTIVITY OF ANTHRACENE AND PHENANTHRENE ON BOTH A LIQUID CRYSTAL AND A VYDAC 201TP STATIONARY PHASE

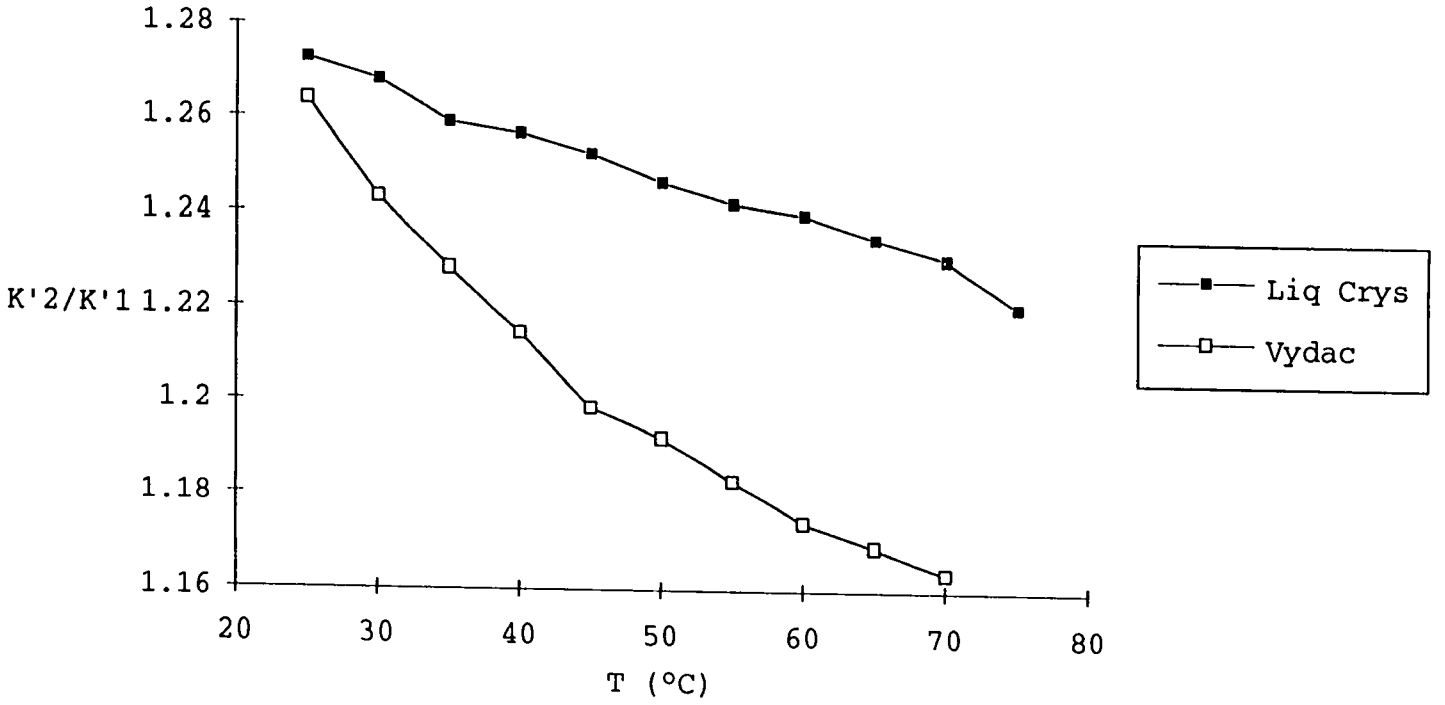


FIGURE 8

RETENTION OF ANTHRACENE AND PHENANTHRENE ON A VYDAC 201TP STATIONARY PHASE, BOTH HEATING AND COOLING

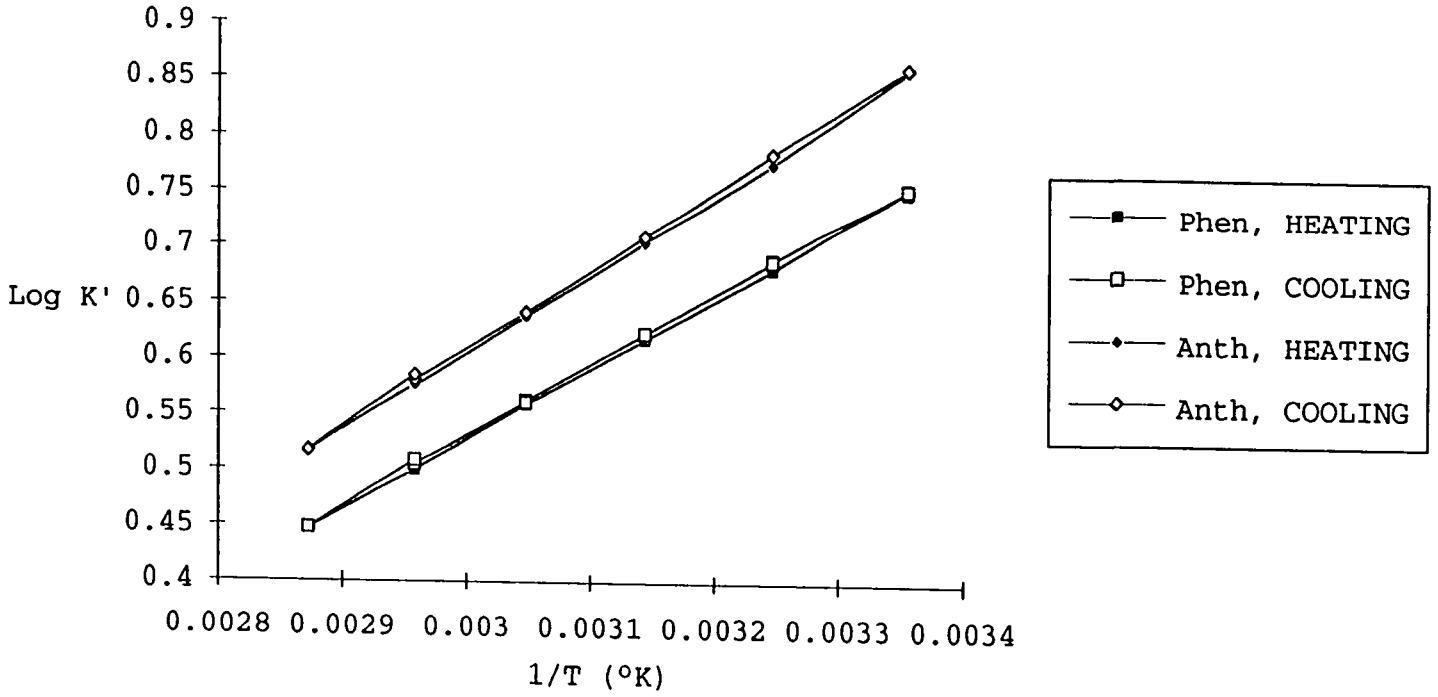


FIGURE 9

SELECTIVITY OF ANTHRACENE AND PHENANTHRENE ON A VYDAC 201TP STATIONARY PHASE, BOTH HEATING AND COOLING

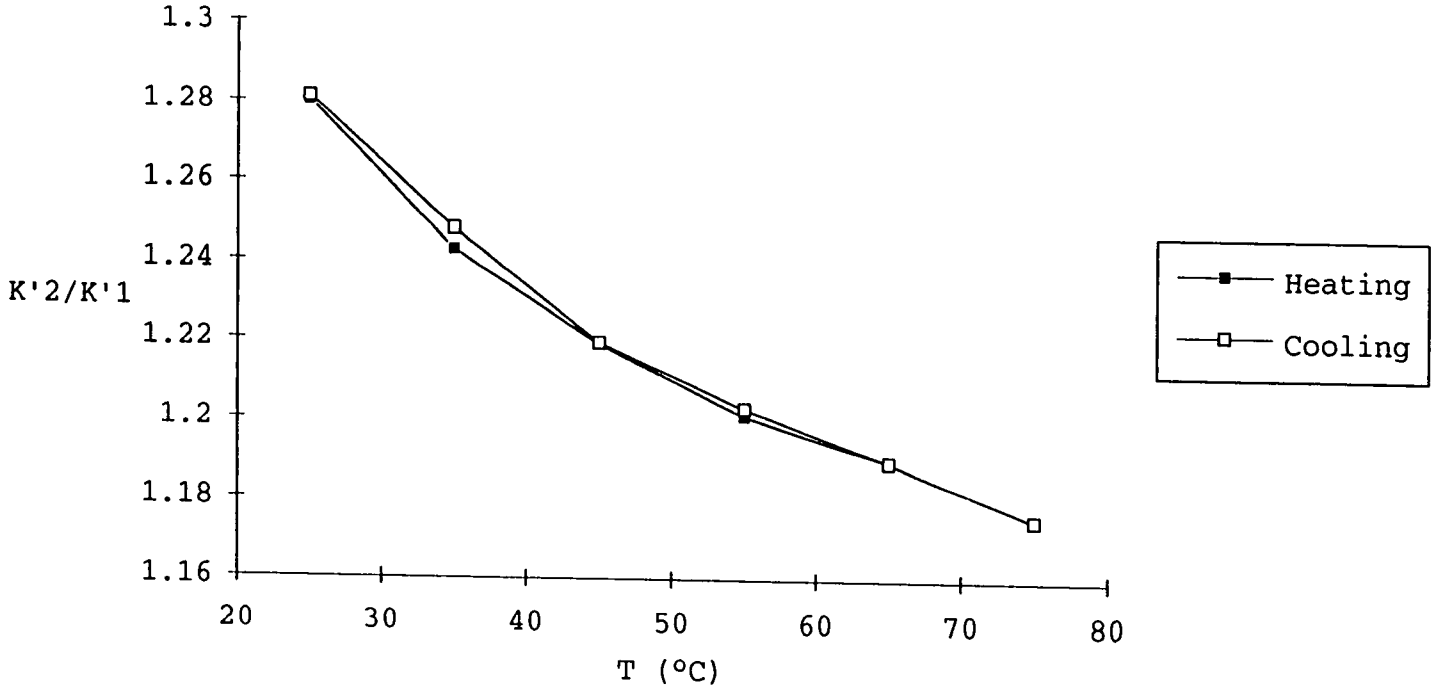


FIGURE 10

RETENTION OF ANTHRACENE ON A LIQUID CRYSTAL STATIONARY PHASE, BOTH HEATING AND COOLING

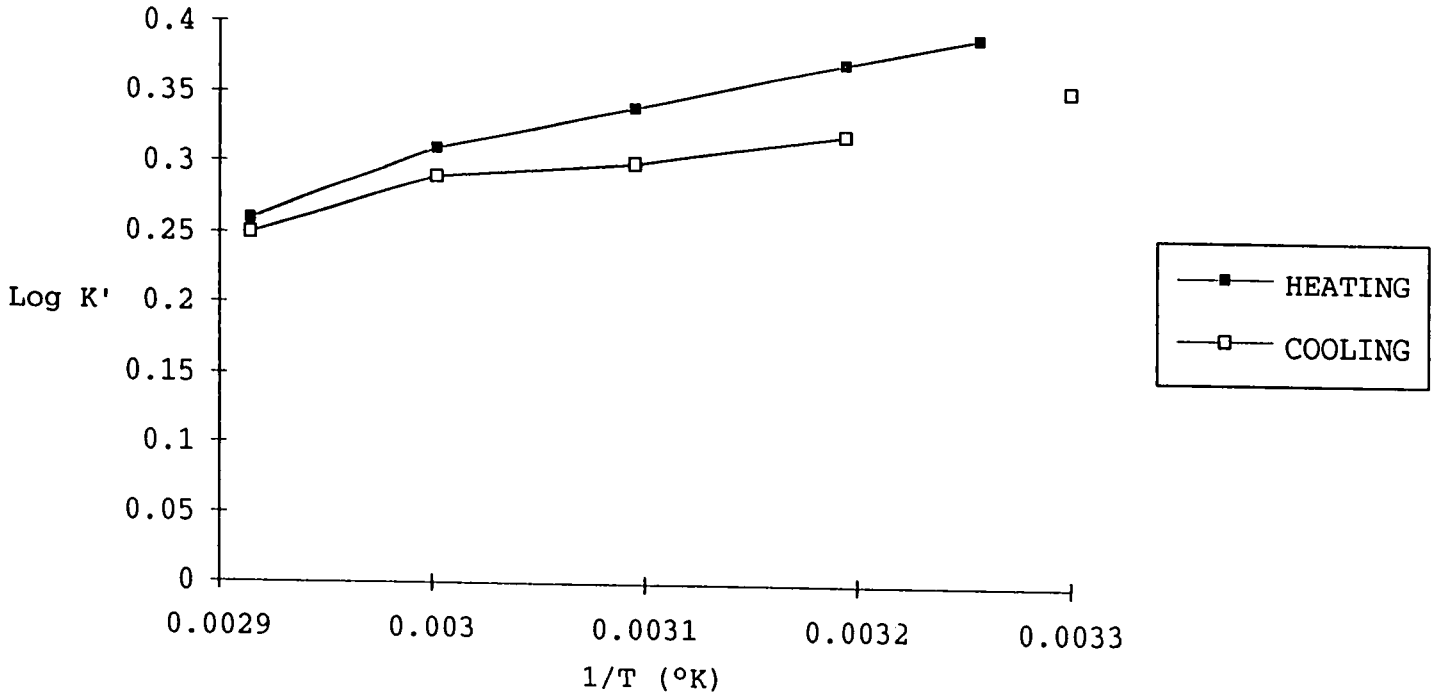
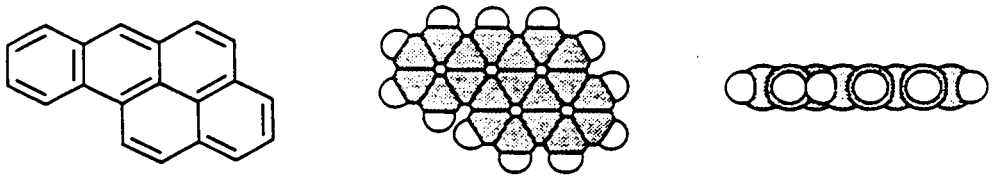
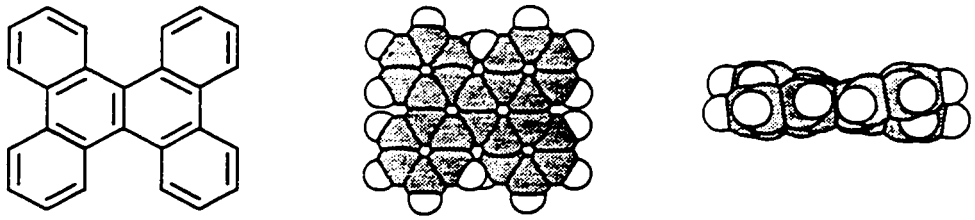


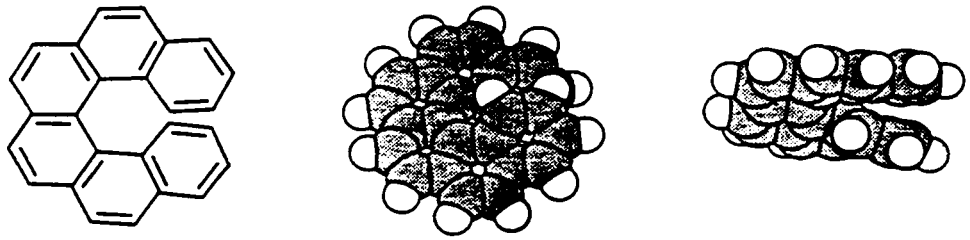
FIGURE 11



BENZO[a]PYRENE



TETRABENZONAPHTHALENE



PHENANTHRO[3,4-c]PHENANTHRENE

FIGURE 12

RETENTION OF PhPh, TBN, AND BaP ON A VYDAC 201TP STATIONARY PHASE

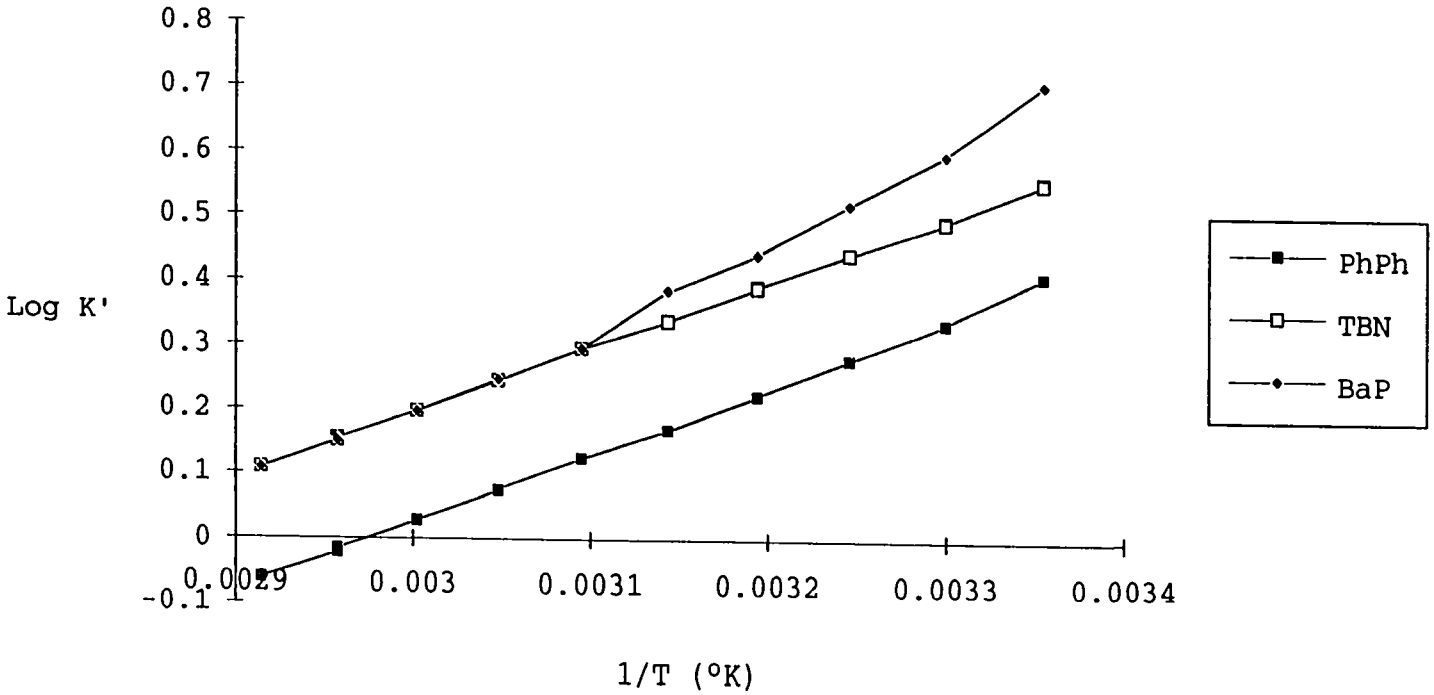


FIGURE 13

SELECTIVITY OF PhPh (1), TBN (2), AND BaP (3) ON A VYDAC 201TP STATIONARY PHASE

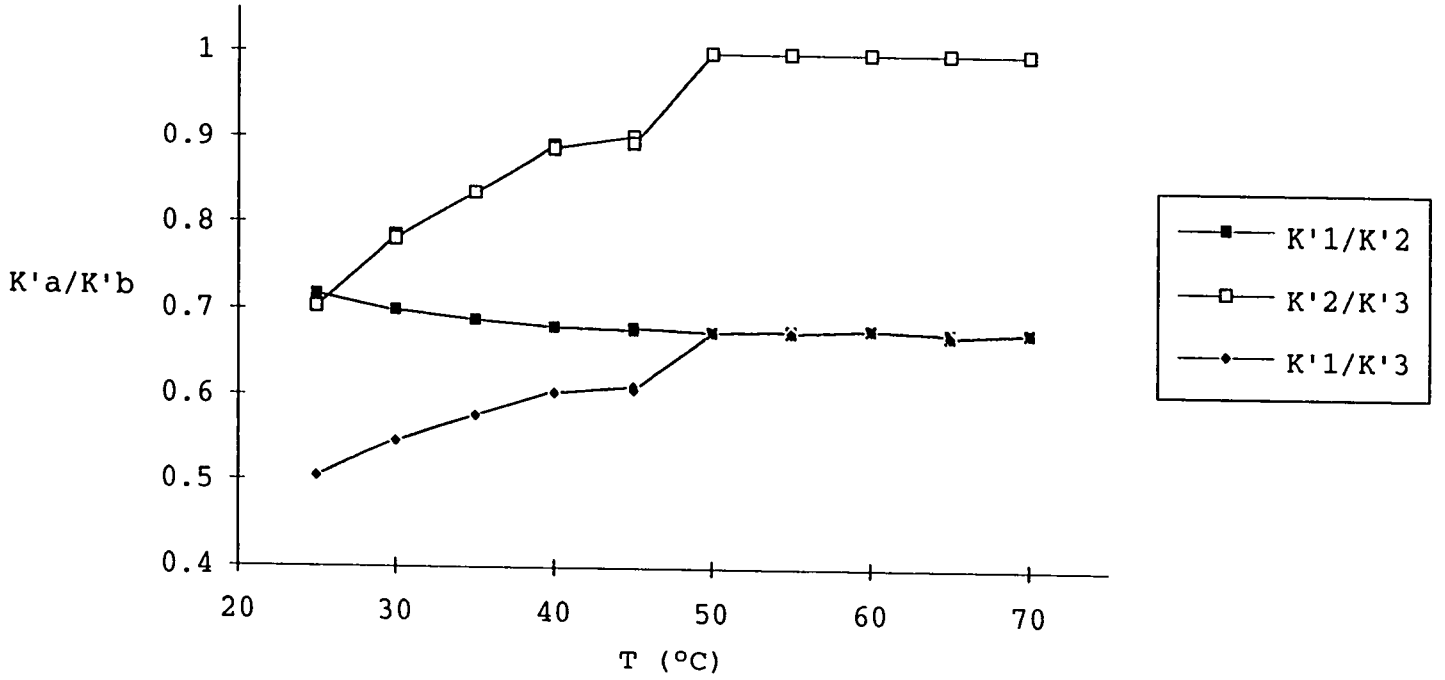


FIGURE 14

TEMPERATURE TEST POINTS ON THE VYDAC 201TP
STATIONARY PHASE

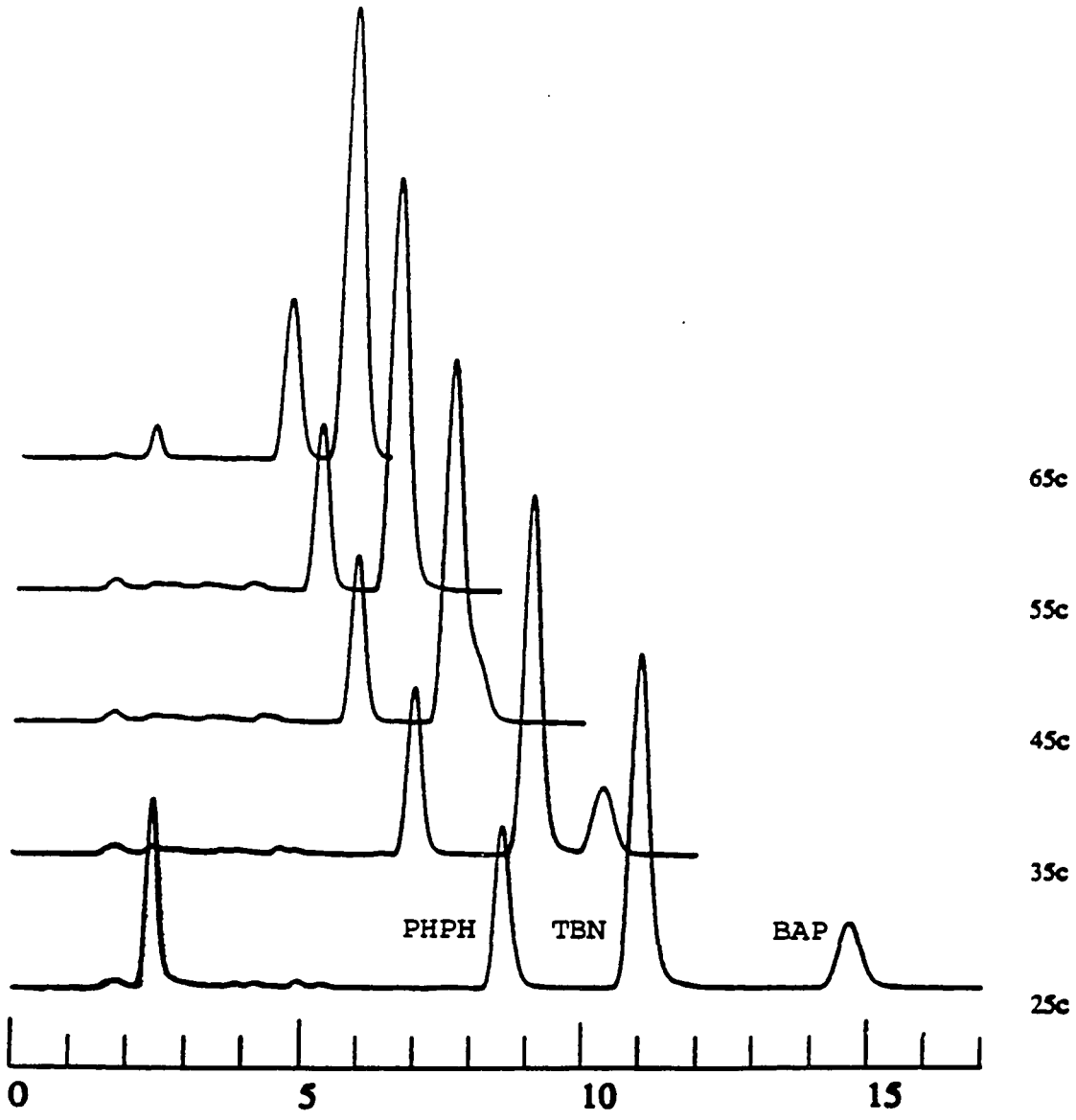


FIGURE 15

RETENTION OF PHENANTHRENE WITH VARYING MOBILE PHASE COMPOSITION

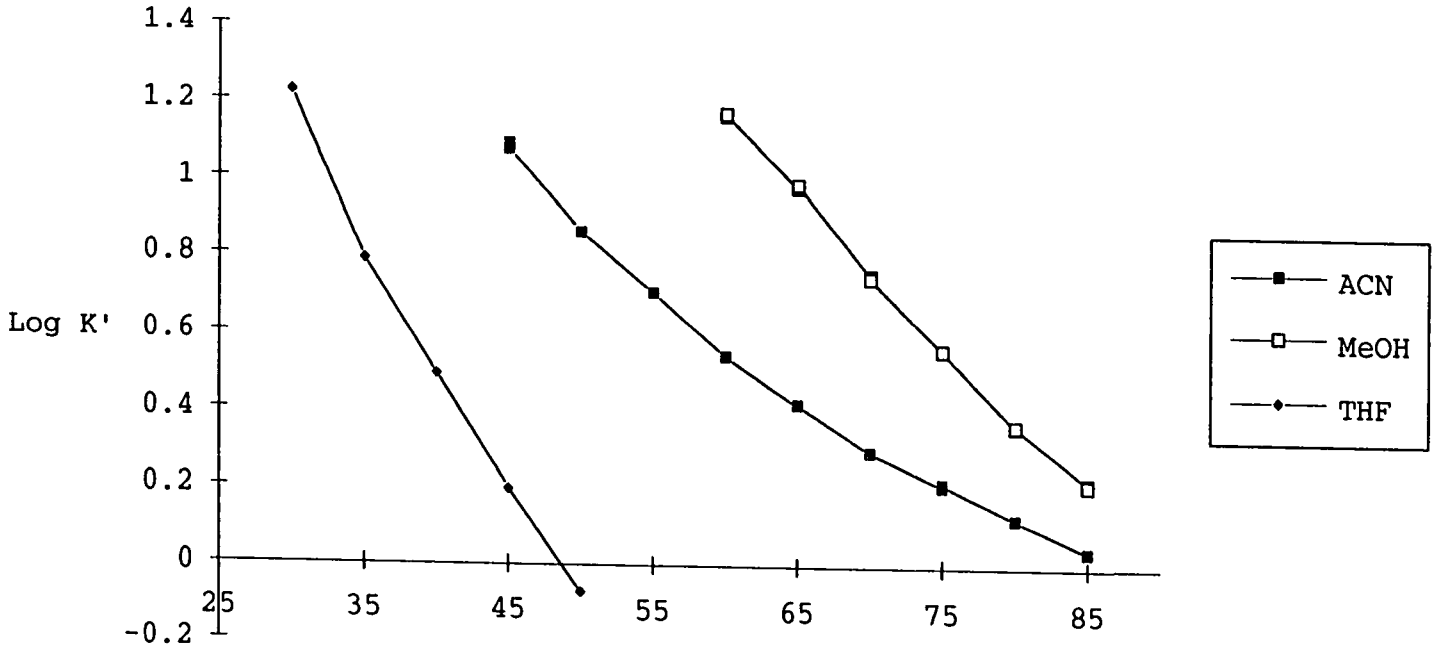


FIGURE 16

RETENTION OF ANTHRACENE WITH VARYING MOBILE PHASE COMPOSITION

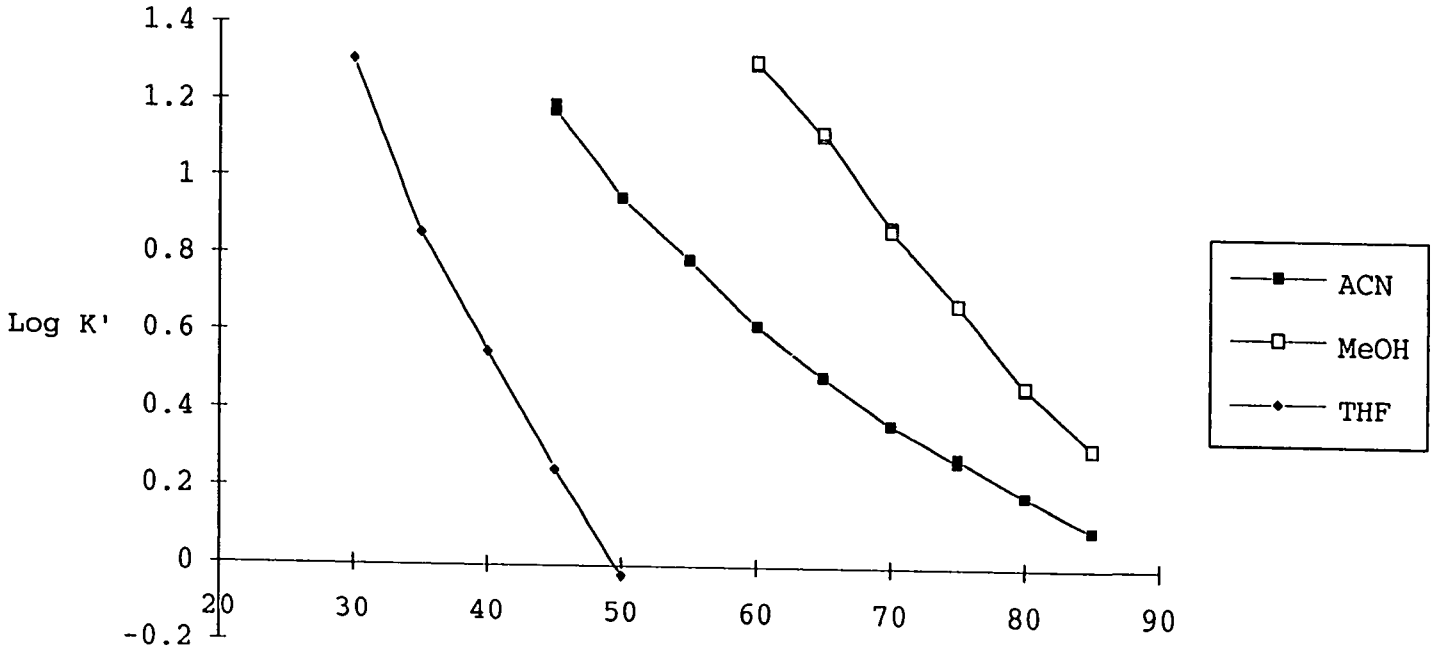
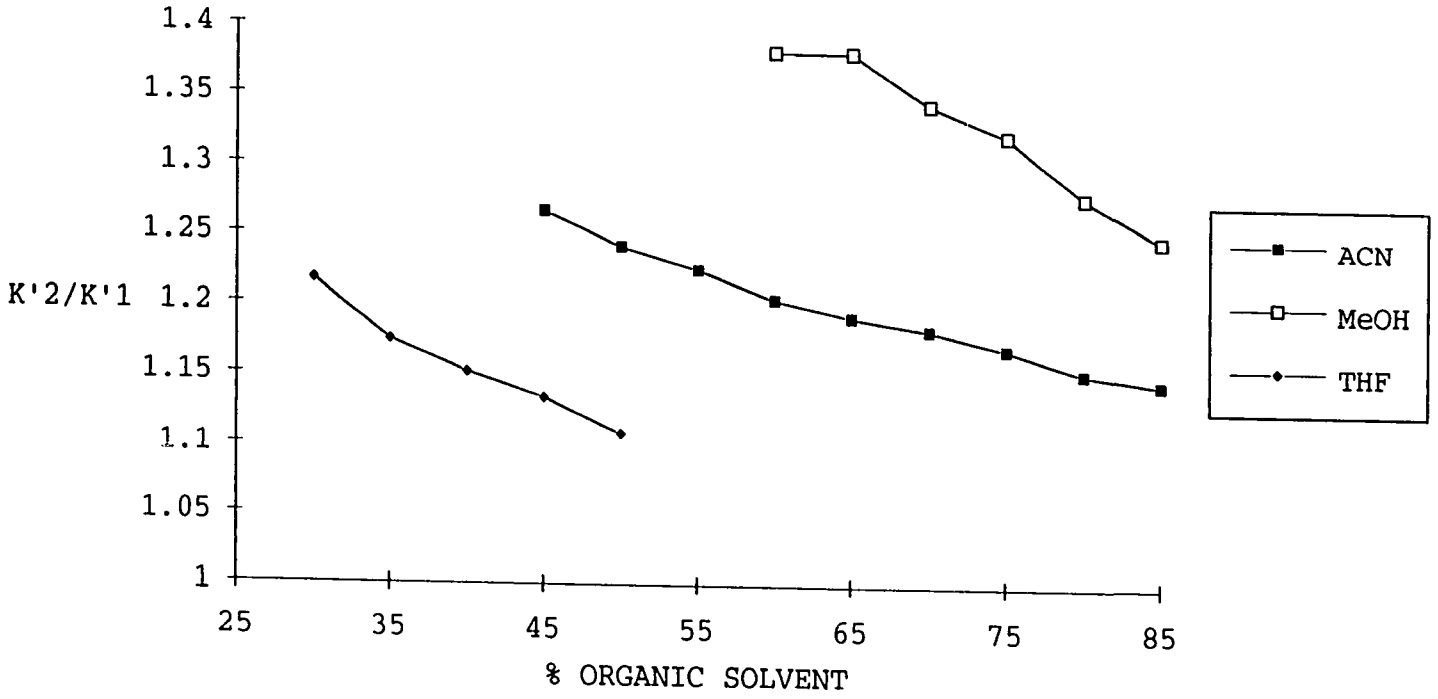


FIGURE 17

SELECTIVITY OF ANTHRACENE AND PHENANTHRENE WITH VARYING MOBILE PHASE COMPOSITION



APPENDIX

Table of Abbreviations

ABMP	[(4-Allyloxy)benzoyloxy]-4-methoxyphenyl
ACN	Acetonitrile
BaP	Benzo[a]pyrene
CP/MAS NMR	Carbon-13 cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy
DRIFT	Diffuse reflectance Fourier transform infrared spectroscopy
DSC	Differential scanning calorimetry
GC	Gas chromatography
HPLC	High performance liquid chromatography
L/B	Length to breadth ratio
LC	Liquid chromatography
MeOH	Methanol
NIST	National Institute of Standards and Technology
ODS	Octadecylsilica
PAH	Polynuclear aromatic hydrocarbons
PhPh	Phenanthro[3,4-c]phenanthrene
SFC	Supercritical fluid chromatography
TBN	1,2:3,4:5,6:7,8-Tetrabenzonaphthalene
THF	Tetrahydrofuran